

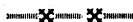
EFFECT OF FLOCCULANTS ON THE SEDIMENTATION OF ORGANIC SOLIDS IN TANNERY UNHAIRING EFFLUENTS*

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ABSTRACT

Procedures were developed for coagulating and flocculating the inorganic and organic suspended solids in lime-sulfide hair-pulping tannery effluents. Inorganic and organic coagulators were added in increasing doses and varying orders of addition to the highly alkaline unhairing wastes (pH 10–12) to determine the largest removal of chemical oxygen demand and suspended organic solids. The coagulators and flocculators effectively reduced the COD by 56 percent, the organic nitrogen by 10–13 percent, the suspended solids by 98 percent, and the volatile suspended solids by 98 percent, respectively.



INTRODUCTION

The primary treatment processes of sanitary (domestic) and industrial wastes are normally divided into unit operations, for example: (a) grit removal, (b) screening, (c) comminution or grinding, (d) plain sedimentation, (e) flocculation, and (f) chemical precipitation. Sedimentation is the removal of suspended solids by gravitational settling of naturally aggregated particles that are heavier than water. When chemicals are added to aid the coalescence of the suspended particles, the process is called coagulation or flocculation.

According to Rideal (1) the concentration of the coagulant, in milligrams of ions per liter necessary to cause coagulation, is called the liminal concentration and may vary with the valence of the coagulator in the proportion 1:2:3. The coagulative powers for the mono-, di-, and trivalent ions are in the proportions of $1 : \frac{1}{x} : \frac{1}{x^2}$, where x is approximately 30. Substituting the value 30 in the proportion and taking the reciprocals yield 1:30:900, the coagulative powers. The polyvalent ions are much more effective as coagulators than the monovalent ions.

Colloidal suspensions have an electrical charge because of preferential adsorption of cations or anions. A positive suspension will be precipitated when an electrolyte containing a readily adsorbable anion is added. When the electrolyte contains a cation that tends to offset the effect of the anion, then the quantity of electrolyte added will vary with the nature of the cation. The quantities of various electrolytes that contain common ions necessary for flocculation will also vary with the nature of the cation or anion.

Tannery lime-sulfide unhairing wastes are complex mixtures: sulfide (S^{2-}), bisulfide (HS^-), calcium ions (Ca^{++}), dissolved albumin, mucoids, mucopolysaccharides, keratin, dissolved and emulsified fats, and insoluble organic and inorganic compounds. The size of particles ranges from a few microns to millimeters, more or less. The net charge of the mixture is positive, possibly owing to the entrainment of impurities by a particular ion present.

The removal of suspended lime-solids from beam house wastes of a sole-leather tannery has been reported by Eye (2), Del Pezzo (3), and Sproul (4). They separated the lime-wastes from the bating-wastes and wash waters, and then treated the lime-wastes with a polyelectrolyte (Rohm and Haas PFA-10)†. Schaffer (5) used Purifloc (Dow Chemical Company) nonionic, anionic, and cationic polyelectrolytes on meat plant wastes and in digesters for sludge thickening, and on metal wastes and combined sewages for settling of suspended solids. The lime-sulfide unhairing unit process contributes 75–80 percent (6) of the biochemical oxygen demand (BOD) and chemical oxygen demand (COD) and a high suspended solids concentration to the beam house effluent. Cooper *et al.* (7) determined that the loading to be applied to a bio-aeration unit would cause a large oxygen deficit, owing to the high concentration of suspended organic and inorganic solids.

This paper reports the use of inorganic coagulants and organic polyelectrolytes for the reduction of organic solids and COD at pH 8 or greater.

METHODS AND RESULTS

Lime-sulfide unhairing effluent was obtained from a side-leather tanner who unhairs fresh hides in a paddle vat by the high-sulfide, hair-pulping process. The concentrated effluent was obtained directly from the unhairing operation and did not include any wash water.

Preliminary experiments were done to determine the liminal concentrations of coagulants and flocculating agents. Individual samples (500 ml.) of unhairing wastes were dosed with inorganic coagulants and organic polyelectrolytes in increasing amounts (0.1, 0.15, 0.2, . . . , 1.00 ml.). Those liminal concentrations which showed the greatest degree of coagulation with the minimum amount of added reagent were chosen for further study.

General Procedure

The effluent was put through a 50 x 50 mesh polypropylene screen, preparatory to flocculation.

One liter samples of screened effluent were transferred to beakers and stirred at 100 r.p.m. with a Phipps & Bird apparatus while reagents were added. When more than one reagent was added, the sample was stirred for five min. after each addition. Controls were run with each experiment. When the reagent addition was completed, stirring velocity was decreased (usually to 25 r.p.m.) to permit floc formation. In most cases, floc formation took place in five minutes. When the floc formed, agitation was stopped and the floc was allowed to settle for 30 minutes. The supernatant was then analyzed for suspended solids, volatile suspended solids, alkalinity, and total nitrogen.

Flocculation of Suspended Solids from Unhairing Wastes at Various pH's Using Ferric Chloride and Alum

Unhairing waste from Tannery A was adjusted from pH 12 to 8 using hydrochloric acid. Nitrogen gas was then bubbled through for 30 minutes to remove hydrogen sulfide gas. Three drops of anti-foam (Dow Chemical Co.) were necessary to stop the foaming due to H_2S production. The solution was tested for H_2S and a trace quantity was found. Six 500 ml. samples of the treated waste were then treated with alum (one percent) and ferric chloride (one percent) in increasing doses, from 0.5 to 3.0 ml. in 0.5 ml. increments, respectively. The ferric chloride treated samples settled immediately when stirring was stopped with the formation of heavy black precipitates due to incomplete removal of sulfide ion. The alum treated samples were stirred for 30 minutes at 100 r.p.m., for five minutes at 40 r.p.m., and then allowed to settle for 30 minutes. The volumes of settleable solids were determined on the alum treated samples at 30 minutes. The results are shown in Table I. Twenty-five ml. of each super-

TABLE I
SETTLEABLE SOLIDS USING ALUM
(30 min.)

	Control	1	2	3	4	5	6
Alum (mg./l.)		8.5	17.0	25.5	34.0	42.5	51.0
Settleable Solids (ml./l.)	200	250	280	220	340	380	350

nate was filtered through #1 Whatman filter paper, and #3 supernate yielded the clearest filtrate. The six alum-dosed samples were treated again with the same dosages of alum as before while stirring at 100 r.p.m. and then at 40 r.p.m.

The solids were settled for 30 minutes and the settleable solids volume measured more than twice the volume of settleable solids after the first treatment, 200–350 ml./l. The #3 sample was given the optimum dosage (25.5 mg./l.).

These results show that heavy doses of alum will flocculate the suspended solids at pH 12.5, but the increase in volume of the solids due to flocculation is more than double the volume of the original solids. Under these conditions the floc density is less than that of the suspending medium and settling does not occur.

Removal of Calcium Ion

Samples were prepared as follows:

Sample (a): an unhairing liquor was prepared containing 1.85 g./l. $\text{Ca}(\text{OH})_2$ + 2 g./l. NaHS. The proteins were extracted from two samples of side leather tannery unhairing wastes from Tannery A and exhaustively dialyzed. *Samples (b) and (c)*: three and one gram quantities of Tannery A protein were dissolved in 1000 ml. of distilled water, respectively. *Sample (d)*: 1000 ml. of Tannery B waste was put through a 65 mesh screen. *Sample (e)*: 1000 ml. of top liquor from a tannery waste that was settled for 30 minutes. *Sample (f)*: seven and one half ml. of one percent sodium hexametaphosphate was added to 1000 ml. of screened Tannery B unhairing waste while stirring at 100 r.p.m. for five minutes, followed by stirring at 25 r.p.m. for five minutes. *Sample (g)*: 9.3 mg./l. sodium hexametaphosphate was added to 1000 ml. of screened Tannery B unhairing waste while stirring at 100 r.p.m. for five minutes, followed by stirring at 25 r.p.m. for five minutes. All of the samples were then dosed simultaneously with 4.65 g. of oxalic acid while stirred at 100 r.p.m. for five minutes, followed by stirring at 25 r.p.m. for five minutes. All samples were then settled for 30 minutes. The data are summarized in Table II.

TABLE II
PRECIPITATION OF CALCIUM FROM LIME-SULFIDE UNHAIRING LIQUOR

Sample	Oxalic Acid (g./l.)	$(\text{NaPO}_3)_6$ (mg./l.)	Precipitate	
			Vol. (ml.)	Type
(a) Lime + NaHS	4.65	0		granular
(b) AP'	4.65	0	0	
(c) 3AP ²	4.65	0	0	
(d) B ³	4.65	0	100	floc (0.5 — 1 mm.)
(e) B supernate	4.65	0	160	floc (0.5 — 1 mm.)
(f) B screened	4.65	7.5	180	floc (1 — 2 mm.)
(g) B screened	4.65	9.3	200	floc (1 — 2.5 mm.)

AP', 3AP² — dialyzed proteins from tannery unhairing liquors.

B supernate — top liquor from settled unhairing liquors.

B screened — unhairing liquors after screening through 65 mesh screens.

B³ — tannery waste as received from Tannery B.

The color of the solution in Sample (a) was the typical yellowish-green, translucent mixture of a paddle vat unhairing waste. The appearance of the solutions in Samples (b) and (c) was the clear yellow color of dissolved hair protein, with no precipitation occurring. In Sample (a), a precipitate formed; however, in the case of Samples (d), (e), (f), and (g) a floc formed. Samples (d) and (e) were clear and green. Samples (b) and (c) showed no pH change because of the initial absence of calcium ion. This experiment proved that calcium ion could be removed without the co-precipitation of dissolved keratin.

Development of Flocs Using Inorganic Electrolytes

To three beakers containing one liter of unhairing liquor (UL) with the composition $(1.85 \text{ g. Ca(OH)}_2 + 2 \text{ g./l. NaHS, pH 12.1})$ the following inorganic compounds were added: #1 sodium hexametaphosphate $(\text{NaPO}_3)_6$ 50 mg./l.; #2 basic magnesium carbonate $[(\text{MgCO}_3)_4\text{Mg(OH)}_2 \cdot n\text{H}_2\text{O}]$, 50 mg./l.; and #3 alum 100 mg./l., respectively; the mixtures were stirred at 100 r.p.m. for ten minutes, and then at 25 r.p.m. for 20 minutes. The contents were allowed to settle for 30 minutes and the suspended solids were determined. Flocs formed with the sodium hexametaphosphate and alum in copious amounts but the settling was poor. The liquor treated with basic magnesium carbonate formed granular particles which settled rapidly.

The three beakers containing the reagents mentioned above were stirred at 100 r.p.m. for 15 minutes and 0.5 mg./l. Primafluc A-10 was added to each. The stirring rate was slowed to 25 r.p.m. for five minutes, and the contents allowed to settle for 30 minutes; then the suspended solids were determined. All three formed heavy flocs which settled within five minutes. There was a marked decrease of the suspended solids in the supernatant, as shown in Table III, when the PFA-10 was added to the respective dosed samples. The percent removal of the suspended solids increased from 53 to 92 $(\text{NaPO}_3)_6$, 32 to 85 (basic magnesium carbonate) and 36 to 80 (alum); the net increase because of the addition of an anionic polyelectrolyte was 39, 53, and 44 percent, respectively.

TABLE III

TREATMENT OF TANNERY UNHAIRING LIQUORS WITH INORGANIC AND ORGANIC POLYELECTROLYTES

Reagent (mg./l.)	Control	Sample #1 $(\text{NaPO}_3)_6$	Sus- pended Solids Removed (%)	Sample #2 Basic Magnesium Carbonate	Sus- pended Solids Removed (%)	Sample #3 Alum	Sus- pended Solids Removed (%)
Suspended Solids	2360	1110	53	1600	32	1500	36
Suspended Solids*		200	92	360	85	480	80

*After the addition of 1.5 mg./l. Primafluc A-10 (PFA-10).

The Effect of Basic Magnesium Carbonate as a Coagulator

Each of three beakers was filled with 1000 ml. of unhairing solution and stirred simultaneously at 100 r.p.m. for 20 minutes. To Sample #1, 50 ml. of basic magnesium carbonate (100 mg./l.) plus 0.5 ml. of PFA-10 were added simultaneously. To Sample #2, 100 ml. of basic magnesium carbonate was added. To Sample #3, 100 ml. of basic magnesium carbonate and 0.5 ml. of PFA-10 were added simultaneously. After five minutes of stirring time, 50 ml. of basic magnesium carbonate was added to Sample #1 and 0.5 ml. of PFA-10 was added to Sample #2. After five additional minutes of stirring time, the velocity was changed to 25 r.p.m. until flocs formed; then the three beakers were allowed to remain quiescent for 30 minutes, after which time the suspended solids were measured. The suspended solids removals were 72, 26, and 77 percent, respectively. The experiment showed that basic magnesium carbonate was not very effective as a coagulant.

Comparison of Anionic and Cationic Polyelectrolytes on Sedimentation of Suspended Solids in Tannery Unhairing Wastes

An experiment was performed to show the effects of cationic and anionic polyelectrolytes on the settleability of suspended solids from a tannery unhairing waste. Increasing doses of anionic and cationic polyelectrolytes were added to screened samples of unhairing wastes. The data in Tables IV-A and IV-B show that the anionic polyelectrolyte PFA-10 is far superior to the cationic electrolytes. The cationic electrolyte C-7 was slightly better at 50 mg./l. dosage than at 3 mg./l. dosage; with this lower value only 16 percent suspended solids was removed. On the other hand, the anionic electrolyte PFA-10 at 3 mg./l. dosage yielded an 83 percent removal of suspended solids.

TABLE-IV-A
COMPARISON OF ANIONIC AND CATIONIC POLYELECTROLYTES FOR
SETTLING SUSPENDED SOLIDS FROM TANNERY UNHAIRING WASTES
(Lower Dosage)

Flocculant	Dosage (mg./l.)	Suspended Solids (mg./l.)	Suspended Solids Settled	
			(mg./l.)	(%)
A Control'		3360		
C*-3	2	2570	790	24
C-3	3	2640	720	21
C-7	2	3320	40	1.2
C-7	3	2820	540	16
PFA**-10	2	1550	1810	54
PFA-10	3	860	2500	74

*C = cationic

**A = anionic

TABLE IV-B

COMPARISON OF ANIONIC AND CATIONIC POLYELECTROLYTES FOR
SETTLING SUSPENDED SOLIDS FROM TANNERY UNHAIRING WASTES
(Higher Dosage)

Flocculant	Dosage (mg./l.)	Suspended Solids (mg./l.)	Suspended Solids Settled	
			(mg./l.)	(%)
B Control ²		2540		
C*-3	12	2440	100	4
C-3	25	2310	230	9
C-7	50	2740	800	32
PFA**-10	3	430	2110	83
PFA-10	5	520	2020	80

*C = cationic

**A = anionic

Effect of the Order of Addition of Electrolytes on the Sedimentation of Suspended Solids in Tannery Unhairing Wastes

The effect of the order of addition on coagulation was tested by adding an anionic polyelectrolyte (PFA-10) first and then adding a cationic polyelectrolyte (C-7); the suspended solids were measured after 30 minutes.

From Table V the best dosage for this order of addition was 2 mg./l. PFA-10 and 0.2 mg./l. of C-7, which gave the greatest removal of suspended solids, 89 percent.

TABLE V

COMPARISON OF THE EFFECT OF THE ORDER OF ADDITION OF
ANIONIC AND CATIONIC POLYELECTROLYTES
(ANIONIC FOLLOWED BY CATIONIC POLYELECTROLYTE)

Dosage (mg./l.)		Suspended Solids (mg./l.)	Suspended Solids Settled	
PFA-10	PFC-7		(mg./l.)	(%)
1.0	0.1	1170	3790	68
2.0	0.2	610	4950	89
3.0	0.3	640	4920	88
4.0	0.4	1150	4410	79
5.0	1.0	1100	4460	80
7.0	1.5	1000	4560	82
14.0		980	4582	82
Control		5560		

The order of addition was repeated using PFA-10 but substituting C-3, another cationic polyelectrolyte, in place of C-7. The percent suspended solids removed increased about ten percent. In Table VI the optimum combination dosages were 3 mg./l. PFA-10 and 0.3 mg./l. C-3, with 93 percent removal of suspended solids.

TABLE VI
COMPARISON OF THE EFFECT OF THE ORDER OF ADDITION OF
ANIONIC AND CATIONIC POLYELECTROLYTES
(ANIONIC FOLLOWED BY CATIONIC POLYELECTROLYTE)

Dosage (mg./l.)		Suspended Solids (mg./l.)	Suspended Solids Settled	
PFA-10	PFC-3		(mg./l.)	(%)
1.0	0.1	1210	5030	81
2.0	0.2	480	5760	92
3.0	0.3	420	5820	93
5.0	0.5	390	5850	94
7.0	1.0	430	5810	93
14.0	1.5	600	5640	90
Control		6240		

The Effect of Reversing the Order of Addition of Polyelectrolytes on the Removal of Suspended Solids

When the cationic polyelectrolyte was added first to the unhairing liquor and, after adequate stirring, the anionic polyelectrolyte was added, the results shown in Table VII were obtained.

TABLE VII
COMPARISON OF THE EFFECT OF THE REVERSE ORDER OF ADDITION
OF ANIONIC AND CATIONIC POLYELECTROLYTES
(CATIONIC FOLLOWED BY AN ANIONIC POLYELECTROLYTE)

Dosage (mg./l.)		Suspended Solids (mg./l.)	Suspended Solids Settled	
C-3	PFA-10		(mg./l.)	(%)
0.1	1.0	2130	3880	65
0.2	2.0	1650	4360	73
0.3	3.0	1750	4260	71
0.4	4.0	1600	4410	73
0.5	5.0	1350	4160	69
0.6	6.0	1850	4160	69
Control		6010		

Comparing the percent solids removal data in Table VI with those of Table VII shows the best removal (94 percent) occurred with the anionic polyelectrolyte added first, followed by the cationic polyelectrolyte. This is 21 percent better than the reverse order of addition, cationic and then anionic polyelectrolyte (73 percent). Further work is in progress to establish the mechanism of this process.

The Effect of Using Organic Polyelectrolytes as Prime Coagulants and Couplers with Inorganic Electrolytes

This experiment was performed to measure the effect on the sedimentation of suspended solids by various dosages of an inorganic polyelectrolyte in the presence of an anionic polyelectrolyte as prime coagulant and a cationic polyelectrolyte as coupler. To each of six samples containing 1000 ml. of a tannery unhairing waste, polyelectrolyte PFA-10 (3 mg./l. dosage) was added first. After five minutes of stirring time at 100 r.p.m., a cationic polyelectrolyte (PFC-3, 0.5 mg./l.) was added and the stirring was continued for an additional five minutes. To Samples 2, 3, 4, 5, and 6 increasing dosages, 20, 40, 60, 80, and 100 mg./l., of sodium hexametaphosphate were added, respectively, and stirred at 100 r.p.m. for five minutes. All six samples were then stirred at 25 r.p.m. for 10 minutes and then allowed to remain quiescent for 30 minutes, after which time the suspended solids in the supernatant were measured. The optimum dosage of sodium hexametaphosphate was 20 mg./l. when added to the coupler as shown in Table VIII. It gave a 94 percent removal of suspended solids. The efficiency declined at higher dosages. The high pH of the unhairing liquor, 12.5, did not interfere with the Primafloc A-10 as the prime coagulant, nor with the Primafloc C-3 as coupler or the sodium hexametaphosphate.

TABLE VIII

THE EFFECT OF ORGANIC PRIME COAGULANTS, COUPLERS,
AND INORGANIC ELECTROLYTES ON THE
SEDIMENTATION OF SUSPENDED SOLIDS

PFA-10	Dosage (mg./l.)		Suspended Solids (mg./l.)	Suspended Solids Settled	
	C-3	(NaPO ₃) ₆		(mg./l.)	(%)
3.0	0.5		1690	6220	79
3.0	0.5	20	500	7410	94
3.0	0.5	40	1510	6400	81
3.0	0.5	60	1120	6790	86
3.0	0.5	80	680	7230	91
3.0	0.5	100	1410	6500	82
Control			7910		

The Effect of Inorganic Polyelectrolytes as Prime Coagulant and Organic Polyelectrolyte as Couplers

The order of addition of PFA-10 as prime coagulant was reversed with sodium hexametaphosphate as coupler. The organic polyelectrolyte concentrations were fixed at 1/10 (C-3) and 1/100 (PFA-10) of the concentration of the sodium hexametaphosphate dosage. The maximum removal with $(\text{NaPO}_3)_6$ as prime coagulant was 91 percent, requiring 20 mg./l. less than when used as a coupler in Table IX.

TABLE IX
THE EFFECT OF USING INORGANIC ELECTROLYTES AS PRIME COAGULANT AND ORGANIC POLYELECTROLYTES AS COUPLERS

$(\text{NaPO}_3)_6$	Dosage (mg./l.)		Suspended Solids (mg./l.)	Suspended Solids Settled	
	C-3	PFA-10		(mg./l.)	(%)
10	0.1	1.0	1940	4070	68
20	0.2	2.0	1575	4435	74
30	0.3	3.0	840	5170	86
40	0.4	4.0	1235	4775	79
50	0.5	5.0	595	5415	90
60	0.6	6.0	565	5445	91
Control			6010		

The Effect of Coagulation and Flocculation on the Removal of Organic Constituents from Lime-Sulfide Unhairing Wastes

A series of experiments was conducted to determine the effect of polyelectrolyte flocculation on the organic composition of tannery unhairing wastes. The graphs in Figure 1 depict the results of adding sodium hexametaphosphate first, followed by a cationic polyelectrolyte, PFC-3, as a coupler, and finally an anionic polyelectrolyte, (PFA-10), as the coagulator. The COD (8) was reduced from 88,738 to 39,893 mg./l. COD, a reduction of 48,845 mg./l. COD, or a 55 percent reduction. The suspended solids were reduced from 13,330 to 180 mg./l., equivalent to a removal of 13,150 mg./l. or 98.6 percent, and the volatile suspended solids were reduced from 9,870 to 168 mg./l., representing a removal of 9,702 mg./l. or 98 percent reduction.

CONCLUSIONS

The experiments using alum as a flocculating agent are not practical because such treatment processes require the lowering of the pH to at least 8 to cause flocculation. Under these conditions, large volumes of H_2S gas are released which

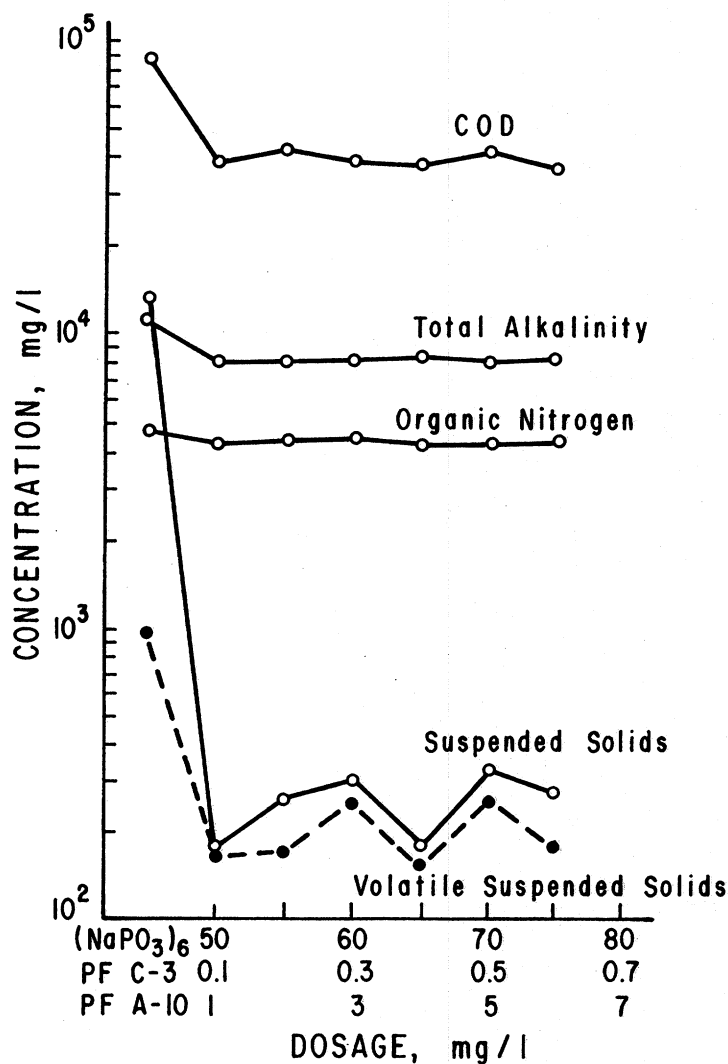


FIGURE 1.—Percent removals of COD, total alkalinity, organic nitrogen, suspended solids, and volatile suspended solids.

are detrimental to personnel. Moreover, the reduction in COD is less than 40 percent. Bench-scale studies on the flocculations of organic and inorganic suspended solids and their sedimentation in highly alkaline tannery lime-sulfide unhairing wastes have shown that these suspended materials may be markedly reduced by 90–98 percent.

The procedure of adding an anionic polyelectrolyte first, followed by a cationic polyelectrolyte, to alkaline unhairing wastes yields a 21 percent better removal

of the suspended solids than the reverse order of addition. Higher removals were obtained when the anionic polyelectrolyte was used as a primary coagulant, followed by the addition of a cationic polyelectrolyte as a coupler and then of an inorganic electrolyte added to form a bridge or network, resulting in large flocculant particles that settle rapidly. The flocculation and eventual sedimentation of the colloidal suspension by polyelectrolytes or inorganic polymers are the result of a sequence of reactions which probably cannot be isolated one from the other. The COD of lime-sulfide unhairing liquors can be reduced by 56 percent and the volatile suspended solids by 98 percent by using the latter procedure.

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